

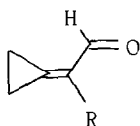
ADDITION REACTIONS TO α -CYCLOPROPYLIDENE KETONES AND ALDEHYDES.

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Abstract. α -Cyclopropylidene ketones show high reactivity towards 1,4-addition reactions.

α -Cyclopropylidene aldehydes 1, aliphatic and aromatic α -cyclopropylidene ketones 2 and α -cyclopropylidene cycloalkanones 3, still unknown in 1977, are now easily available either by photooxygenation of enol ethers of cyclopropyl ketones, followed by PPh_3 reduction (1) (1) or, better, by Wittig reaction of cyclopropylidene-triphenylphosphorane with α -keto- or α -aldoacetals followed by desacetalisation with moist silicagel (1, 2a-c, 3) (2).

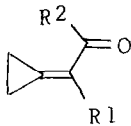


1a R = H

1b Me

1c Ph

1d cyclopropyl



2a R1 = H R2 = Me

2b R1 = R2 = Me

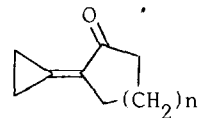
2c R1 = H R2 = Ph

2d R1 = Me R2 = Ph

2e R1 = R2 = Ph

2f R1 = cyclopropyl R2 = Me

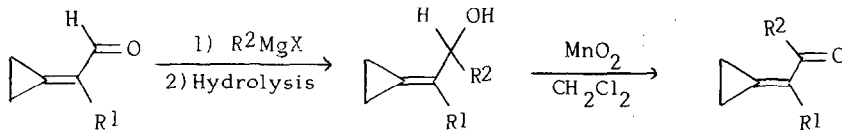
2g R1 = R2 = cyclopropyl



3a n = 1

3b 2

Some ketones (e.g. 2d-g) are more easily obtained by the reaction of aldehydes 1 with Grignard reagents (which leads exclusively to the 1,2 addition product), followed by oxidation with active MnO_2 (3).



Examples

1a

88%¹ R1 = Me R2 = Ph

2d 81%¹

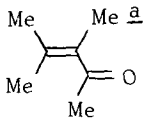
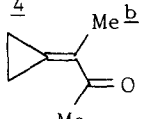
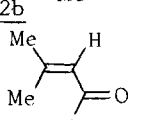
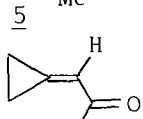
1d

62%¹ R1 = R2 = cyclopropyl

2g 50%¹

¹ yield of isolated product

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Reactions	Results after hydrolysis
 <u>4</u> + Me ₂ CuLi	21% 1,4 addition product 72% enolisation (recovered enone) (4)
 <u>2b</u> + Me ₂ CuLi	67% 1,4 addition product (the sole isolated product)
 <u>5</u> + MeMgI	61% 1,2 addition product (5) (the sole isolated product)
 <u>2a</u> + MeMgI	1,2/1,4 addition products = 75/25 (sum of yields 60%)

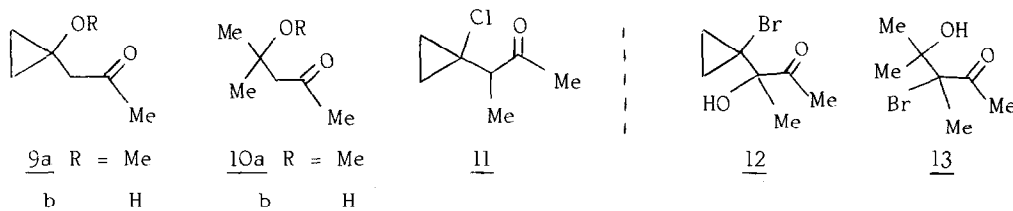
a Polarographic reduction potential (6) -2.30 V (litt. -2.35 V (4))

b Polarographic reduction potential (6) -2.00 V.

Table I. - 1,2 and 1,4 addition reactions of Me₂CuLi and MeMgI with α -isopropylidene and α -cyclopropylidene ketones.

MeOH (2 equivalents) the same ketone gives the alcohol 8 only (77% yield of isolated product). Interestingly NaBH₄-CeCl₃ in MeOH (7) (1 equivalent) yields only the 1,2 addition product 6 (90% yield of isolated product) ; similar results are obtained with other α -cyclopropylidene ketones (see the following communication (8)).

α -Cyclopropylidene ketones quickly add MeOH, H₂O and HCl. For example at 25°, in MeOH containing 0,5% KOH (w/v) cyclopropylidene-acetone 2a was instantaneously transformed into the β -methoxy-cyclopropylacetone 9a (69% yield of isolated product) ; mesityl oxide reacts much more slowly : 7 h at 25° were necessary



to obtain a 70% conversion into 10a. Addition of water (5.5% COOH-COOH, H₂O, DMSO at 25°) is also slower to 5 than to 2a : 10 h are required to obtain an only 30% conversion of 5 into 10b while the complete disappearance of 2a only needs 3 h (yield

of isolated 9b : 65%). 3-Cyclopropylidene 2-butanone 2b instantaneously adds HCl (in CCl_4 at 25°) and yields 3-(1'-chloro cyclopropyl)2-butanone 11 (87% yield of isolated product).

BrOH addition (with NBS, DMSO, H_2O - the reaction starts with the attack of the double bond by a bromonium ion (9)) to α -cyclopropylidene ketones is also interesting. 3,4-Dimethyl 3-penten 2-one 4 gives the expected result : the sole isolated product is the β -hydroxy α -bromo ketone 13 (66% yield). The opposite is true for the α -cyclopropylidene ketone 2b : the only isolated product (47% yield) is the α -hydroxy β -bromo ketone 12 beside resinous compounds.

These analogies and differences between α -cyclopropylidene ketones and regular α -enones can be used to advantage in synthetic work : some applications are in progress (8).

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